FULL DIMENSIONAL ROVIBRATIONAL VARIATIONAL CALCULATIONS OF THE S_1 STATE OF C_2H_2

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Rovibrational variational calculations on global potential energy surfaces are often essential for investigating large amplitude vibrational motion and isomerization between multiple stable conformers, as well as for understanding the spectroscopic signatures of such dynamics. The efficient and accurate representation of high dimensional potential energy surfaces and the diagonalization of large rovibrational Hamiltonians make these calculations a technically non-trivial task.

The first excited singlet electronic state of acetylene (C_2H_2) is an ideal model isomerizing system. The S_1 state supports both a *trans* conformer and a higher energy *cis* conformer ($T_e^{cis} - T_e^{trans} \approx 2700\ \mathrm{cm}^{-1}$), separated by a planar near-half-linear transition state ($T_e^{TS} - T_e^{trans} \approx 5000\ \mathrm{cm}^{-1}$). The low-energy structure of the *trans* well is complicated by strong Coriolis and Darling-Dennison interactions between the near-resonant torsion and asymmetric bending modes. The resulting polyad patterns are eventually broken as the internal vibrational energy approaches that of the barrier to isomerization. In this region, qualitatively new spectroscopic patterns emerge, such as rotational K-staggering and vibrational effective frequency dips.

We examine these effects with an efficient *ab initio* variational treatment. Our global potential energy surface is constructed as a hybrid of a high-level reduced dimension surface, which excludes the two r_{CH} bond lengths, and a lower-level full dimensional surface incorporating the effects of r_{CH} displacement. Diagonalization of the large, sparse Hamiltonian, which contains an exact internal coordinate rovibrational kinetic energy operator, is achieved with an efficient restarted Lanczos algorithm that generates variational energies and wavefunctions. We discuss how our results elucidate the S_1 state's rich variety of spectroscopic features and the insights they provide into the isomerization process.